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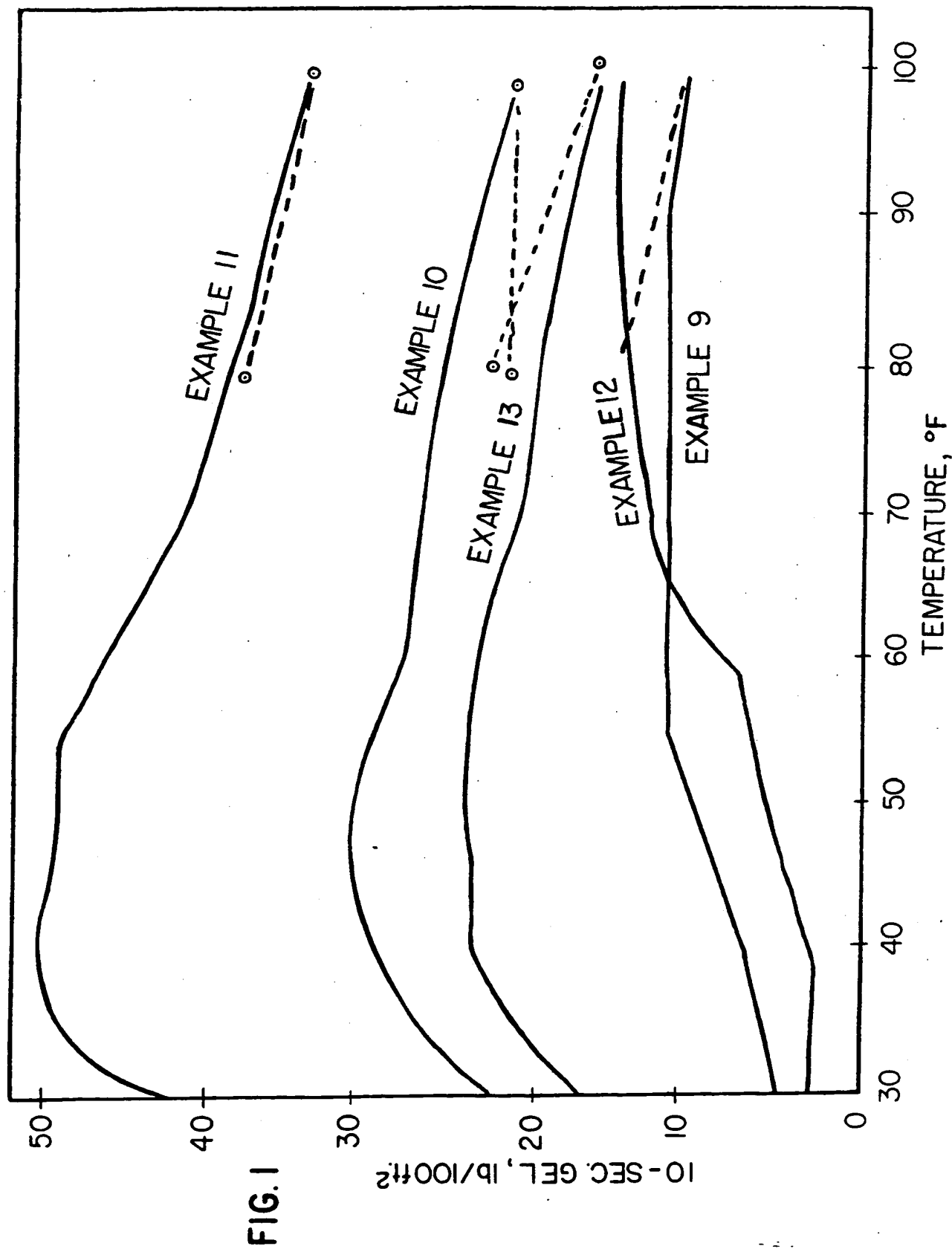
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(54) Oil Base Fluids with
Organophilic Clays

(57) An oil base fluid containing an organophilic clay gellant is disclosed. The gellant is the reaction product of an organic cationic compound, an organic anionic compound and a smectite-type clay.

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SPECIFICATION

Oil Base Fluids Containing Cationic Organophilic Clays

This invention relates to organophilic organic-clay complexes which are dispersible in organic liquids to form a gel therein. More particularly such gels are useful in oil base muds and oil base packer fluids.

It is well known that organic compounds containing a cation will react with clays which contain a negative layer-lattice and exchangeable cations to form organophilic organic-clay products. The reaction of an organic cation containing at least one alkyl group of at least 10 carbon atoms with clay generally results in organo-clays swellable in certain organic liquids.

Prior publications include U.S. Pat. No. 2,531,427, and U.S. Pat. No. 2,966,506, both incorporated herein by reference, and the book "Clay Mineralogy", 2nd Edition, 1968 by Ralph E. Grim (McGraw Hill Book Co., Inc.), particularly Chapter 10, Clay-Mineral-Organic Reactions; pp. 356—368—Ionic Reactions, Smectite; and pp. 392—401—Organophilic Clay-Mineral Complexes.

Maximum gelling (thickening) efficiency from these organoclays is achieved by adding a low molecular weight polar organic dispersing material to the composition. Such materials are disclosed in U.S. Patents: O'Halloran 2,677,661; McCarthy et al. 2,704,276; Stratton 2,833,720; Stratton 2,879,229; and Stansfield et al. 3,294,683. The use of such dispersion aids was found unnecessary when using particular organophilic clays derived from substituted quaternary ammonium compounds as disclosed in Finlayson et al 4,105,578 and Finlayson 4,208,218.

Prior organophilic clays have exhibited limited broad range gelling utility due to fluctuating dispersion and viscosity properties. While the materials disclosed in U.S. Patent 4,105,578 have not shown such deficiencies, such materials are difficult and costly to produce.

Summary of the Invention

An oil-base fluid of this invention which comprises an oil phase and from about 1 to about 50 lbs. per barrel of the fluid of an organophilic gellant comprising the reaction product of an organic cationic compound, an organic anionic compound and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay.

Detailed Description of the Invention

The oil base fluid of the present invention consists of an oil phase and from about 1 to about 50 lbs. per barrel of fluid of an organophilic clay gellant. Preferably, the fluid is non-aqueous. A suitable oil phase of this invention may be crude petroleum and fractions thereof, including but not limited to diesel oil, kerosene, fuel oil, light lubricating oil fractions, and heavy naphtha having a boiling range between about 300°F to about 600°F. The preferred oil phase material is diesel oil.

The amount of the organophilic clay employed should be effective to obtain the necessary degree of gellation (thickening) of the oil-base fluid for the intended application, that is, drilling fluid or packer fluid. The minimum concentration of organophilic clay needed to gel a particular fluid is dependent upon factors such as the type of organophilic clay used, the characteristics of the oil phase, the maximum temperature to which the fluid is to be raised, and the type of emulsifier, if any. The maximum concentration of organophilic clay is limited to that which will form a pumpable fluid.

The concentration of organophilic clay within the range of about 1 to about 50 lbs. per barrel (42 gallon barrel of fluid) will generally provide a sufficiently gelled fluid for broad applications. Preferably about 1 to about 10 lbs. per barrel are employed in the preparation of oil-base drilling fluids whereas amounts from about 6 to 50 lbs. per barrel have been found adequate for the preparation of oil-base packer fluids. It has been found that when the organophilic clay is mixed into the oil-base fluid, essentially complete gelling is achieved at low shear mixing. The resulting oil-base fluid is a stable oil-base fluid at surface temperatures below -20°F and downhole temperatures up to 500°F. The formation of the stable fluid occurs in a matter of minutes following addition and low shear mixing of the organophilic clay in the oil base fluid.

A packer fluid is prepared in accordance with this invention by adding to an oil medium the organophilic clay. The composition of the packer fluid is regulated as discussed above to provide a pumpable composition. Optional emulsifiers, weighting agents, and fluid loss control materials may be added at any time. Once prepared, the packer fluid is transferred, such as by pumping, into a well bore, at least one portion of which is to be insulated.

The oil-base fluid can be prepared and used either before drilling commences or while drilling is in progress. The method of adding the ingredient to prepare the fluid is not critical. Mixing is accomplished with conventional devices capable of developing a low shear mixing force. Greater mixing force may be employed even though not necessary. Once prepared, the emulsion drilling fluid is transferred, such as by pumping, into a well bore and circulated to the bit and through the borehole in contact with the walls thereof.

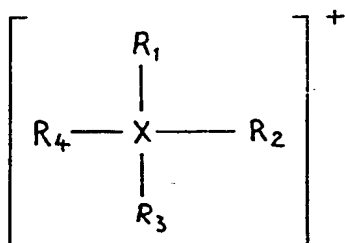
The organophilic clays of this invention can be prepared by admixing the clay, organic cation, organic anion and water together, preferably at a temperature within the range from 20°C. to 100°C., more preferably 35°C. to 77°C. for a period of time sufficient for the organic cation and organic anion

complex to intercalate with the clay particles. The mixing step is followed by filtering, washing, drying and grinding. The addition of the organic cation and organic anion may be done either separately or as a complex. In using the organophilic clays in emulsions, the drying and grinding steps may be eliminated. When admixing the clay, organic cation, organic anion and water together in such concentrations that a slurry is not formed, filtration and washing steps can be eliminated.

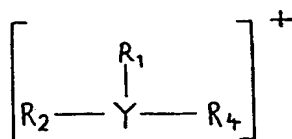
The organophilic clays of the invention may also be prepared by admixing the organic anion with an aqueous clay slurry preferably at a temperature between 20°C. and 100°C. for a sufficient time to prepare a homogeneous mixture followed by the addition of the organic cation in sufficient amounts to satisfy the cation exchange capacity of the clay and the cationic capacity of the organic anion. The mixture is reacted with agitation at a temperature between 20°C. and 100°C. for a sufficient time to allow the formation of an organic cation-organic anion complex which is intercalated with the clay and the cation exchange sites of the clay are substituted with the organic cation. Reaction temperatures below 20°C or above 100°C, are not preferred due to the need for additional processing equipment.

The organic cationic compounds useful in this invention may be selected from a wide range of materials that are capable of forming an organophilic clay by exchange of cations with the smectite-type clay. The organic cationic compound should have a positive charge localized on a single atom or on a small group of atoms within the compound. Preferably the organic cation is selected from the group consisting of quaternary ammonium salts, phosphonium salts, sulfonium salts and mixtures thereof wherein the organic cation contains at least one linear or branched alkyl group having 8 to 60 carbon atoms. More preferably, the organic cation contains one member selected from a first group consisting of a β,γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, and an aralkyl group and mixtures thereof and a second member selected from a second group consisting alkyl group. More preferably, two additional members of the compound are individually selected from a third group consisting of a β,γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, an aralkyl group, an alkyl group having from 1 to 22 carbon atoms and mixtures thereof.

The organic cation may be selected from a group consisting of the formulae:



and



wherein X is nitrogen or phosphorus, Y is sulfur, R_1 is an alkyl group having 8 to 60 carbon atoms; and R_2 , R_3 and R_4 are individually selected from the group consisting of hydrogen; hydroxyalkyl groups having 2 to 6 carbon atoms; alkyl groups containing 1 to 22 carbon atoms; aryl groups; aralkyl groups containing 1 to 22 carbon atoms on the alkyl chain; and mixtures thereof. Preferably, X is nitrogen.

35 R_1

The long chain alkyl radical may be branched or unbranched, saturated or unsaturated, substituted or unsubstituted and should have from 8 to 60 carbon atoms in the straight chain portion of the radical. Preferably, R_1 is an alkyl group having 12 to 60 carbon atoms. More preferably, R_1 is an alkyl group having 12 to 22 carbon atoms.

40 The long chain alkyl radicals may be derived from naturally occurring oils including various vegetable oils, such as corn oil, coconut oil, soybean oil, cottonseed oil, and castor oil and various animal oils and fats such as tallow oil. The alkyl radicals may be derived synthetically from sources such as alpha olefins.

45 Representative examples of useful branched, saturated alkyl radicals include 12-methylstearyl; and 12-ethylstearyl. Representative examples of useful branched, unsaturated radicals include 12-methyloleyl and 12-ethyloleyl. Representative examples of unbranched saturated radicals include lauryl; stearyl; tridecyl; myristal (tetradecyl); pentadecyl; hexadecyl; hydrogenated tallow and

docosonyl. Representative examples of unbranched, unsaturated and unsubstituted long chain alkyl radicals include oleyl, linoleyl; linolenyl, soya and tallow.

R₂, R₃, R₄

5 R₂, R₃, and R₄ are individually selected from the group consisting of hydrogen; a hydroxyalkyl group having 2 to 6 carbon atoms; an alkyl group containing 1 to 22 carbon atoms; an aryl group; an aralkyl group containing 1 to 22 carbon atoms in the alkyl chain of the aralkyl group, and mixtures thereof. 5

10 Preferably, R₂ is selected from a group consisting of a β,γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, and a aralkyl group containing 1 to 22 carbon atoms in the alkyl chain of the aralkyl group and mixtures thereof. Preferably 10 R₃ and R₄ are individually selected from a group consisting of a β,γ -unsaturated alkyl group, a hydroxyalkyl group having 2 to 6 carbon atoms, an alkyl group having 1 to 22 carbon atoms, an aralkyl group which includes benzyl and substituted benzyl moieties including fused ring moieties having linear or branched chains of 1 to 22 carbon atoms in the alkyl portion of the aralkyl group and mixtures thereof. 15

20 The hydroxyalkyl group may be selected from a hydroxyl substituted aliphatic radical having from 2 to 6 aliphatic carbons wherein the hydroxyl is not substituted at the carbon adjacent to the positive charged atom. The alkyl group may be substituted with an aromatic ring. Representative examples include 2-hydroxyethyl; 3-hydroxypropyl; 4-hydroxypentyl; 6-hydroxyhexyl; 2-hydroxypropyl; 2-hydroxybutyl; 2-hydroxypentyl; 2-hydroxyhexyl; 2-hydroxycyclohexyl; 3-hydroxycyclohexyl; 4-hydroxycyclohexyl; 2-hydroxycyclopentyl; 3-hydroxycyclopentyl; 2-methyl-2-hydroxypropyl; 3-methyl-2-hydroxybutyl; and 5-hydroxy-2-pentenyl. 20

25 The alkyl group containing 1 to 22 carbon atoms may be linear or branched, cyclic or acyclic, substituted or unsubstituted. Representative examples of useful alkyl groups include methyl; ethyl; propyl; 2-propyl; iso-butyl; cyclopentyl; and cyclohexyl. 25

30 The alkyl radicals may be derived from sources similar to the long chain alkyl radical, R₁, above. The preferred β,γ -unsaturated alkyl group may be cyclic or acyclic, unsubstituted or substituted. β,γ -unsaturated alkyl radicals preferably contain less than 7 aliphatic carbon atoms. Aliphatic radicals substituted on the β,γ -unsaturated group preferably containing less than 4 carbon atoms. The β,γ -unsaturated alkyl radical may be substituted with an aromatic ring that is conjugated with the unsaturation of the β,γ moiety. The β,γ radical may also be substituted both with aliphatic radicals and aromatic rings. 30

35 Representative examples of cyclic β,γ -unsaturated alkyl groups include 2-cyclohexenyl and 2-cyclopentenyl. Representative examples of acyclic β,γ -unsaturated alkyl groups containing 6 or less carbon atoms include propargyl; 2-propenyl; 2-butenyl; 2-pentenyl; 2-hexenyl; 3-methyl-2-butenyl; 3-methyl-2-pentenyl; 2,3-dimethyl-2-butenyl; 1,1-dimethyl-2-propenyl; 1,2-dimethyl-2-propenyl; 2,4-pentadienyl; and 2,4-hexadienyl. Representative examples of acyclic-aromatic substituted compounds include 3-phenyl-2-propenyl; 2-phenyl-2-propenyl; and 3-(4-methoxy phenyl)-2-propenyl. 35 Representative examples of aromatic and aliphatic substituted materials include 3-phenyl-2-cyclohexenyl; 3-phenyl-2-cyclopentenyl; alkyl group may be substituted with an aromatic ring. 40

40 Examples of aryl groups would include phenyl such as in N-alkyl and N,N-dialkyl anilines, wherein the alkyl groups contain between 1 to 22 carbon atoms; ortho-, meta- and para-nitrophenyl, ortho-, meta- and para-alkyl phenyl, wherein the alkyl group contains between 1 and 22 carbon atoms, 2-, 3-, 4- halophenyl wherein the halo group is defined as chloro, bromo, or iodo, and 2-, 3-, and 4-carboxyphenyl and esters thereof, where the alcohol of the ester is derived from an alkyl alcohol, wherein the alkyl group contains between 1 and 22 carbon atoms, aryl such as a phenol, or aralkyl such as benzyl alcohols; fused ring aryl moieties such as naphthalene, anthracene, and phenanthrene. 45

50 Representative examples of an aralkyl group, include benzyl and those materials derived from compounds such as benzyl halides, benzhydryl halides, trityl halides, 1-halo-1-phenylalkanes wherein the alkyl chain has from 1 to 22 carbon atoms such as 1-halo-1-phenylethane; 1-halo-1-phenylpropane; and 1-halo-1-phenyloctadecane; substituted benzyl moieties such as would be derived from ortho-, meta- and para-chlorobenzyl halides, para-methoxybenzyl halides; ortho-, meta- and para-nitrobenzyl halides, and ortho-, meta- and para-alkylbenzyl halides wherein the alkyl chain contains from 1 to 22 carbon atoms; and fused ring benzyl-type moieties such as would be derived from 2-halomethylnaphthalene, 9-halomethylanthracene and 9-halomethylphenanthrene, wherein the halo group would be defined as chloro-, bromo-, iodo-, or any other such group which serves as a leaving group in the nucleophilic attack of the benzyl type moiety such that the nucleophile replaces the leaving group on the benzyl type moiety. 55

60 A compound is formed of the above described organic cation and an anionic radical which is selected from the group consisting of chloride, bromide, iodide, nitrite, hydroxide, acetate, methyl sulfate and mixture thereof. Preferably the anion is selected from the group consisting of chloride and bromide, and mixtures thereof, and is more preferably chloride, although other anions such as iodide, acetate, hydroxide, nitrite, etc., may be present in the organic cationic compound to neutralize the cation. 60

Organic cationic salts may be prepared by methods as disclosed in U.S. 2,355,356, 2,775,617 and 3,136,819.

The organic anions useful in this invention should be capable of reacting with an organic cation and form intercalations with a smectite-type clay as an organic cation-organic anion complex. The molecular weight (gram molecular weight) of the organic anion is preferably 3,000 or less, and most preferably 1,000 or less and contains at least one acidic moiety per molecule as disclosed herein. The organic anion is preferably derived from an organic acid having a pK_A less than about 11.0. As indicated, the source acid must contain at least one ionizable hydrogen having the preferred pK_A in order to allow the formation of the organic cation-organic anion complex and subsequent intercalation reaction to occur.

Also useable is any compound which will provide the desired organic anion or hydrolysis.

Representative compounds include:

1) acid anhydrides including acetic anhydride, maleic anhydride, succinic anhydride and phthalic anhydride;

2) acid halides including acetyl chloride octanoyl chloride, lauroyl chloride, lauroyl bromide and benzoyl bromide;

3) 1,1,1-trihalides including 1,1,1-trichloroethane and 1,1,1-tribromooctane; and

4) orthoesters including ethyl orthoformate, and ethyl orthostearate.

The organic anions may be in the acid or salt form. Salts may be selected from alkali metal salts, alkaline earth salts, ammonia, and organic amines. Representative salts include: hydrogen, lithium, sodium, potassium, magnesium, calcium, barium, ammonium and organic amines such as ethanolamine, diethanolamine, triethanolamine, methyl diethanolamine, butyl diethanolamine, diethyl amine, dimethyl amine, triethyl amine, dibutyl amine, and mixtures thereof. The preferred alkali metal salt is sodium.

Suitable acidic functional organic compounds include:

1) Carboxylic acids including:

(a) benzenecarboxylic acids such as benzoic acid, ortho- meta- and para-phthalic acid, 1,2,3-benzene tricarboxylic acid; 1,2,4-benzenetricarboxylic acid; 1,3,5-benzenetricarboxylic acid; 1,2,4,5-benzene tetracarboxylic acid; 1,2,3,4,5,6-benzenehexacarboxylic acid (mellitic acid);

(b) alkyl carboxylic acids having the formula $H-(CH_2)_n-COOH$, wherein n is a number from 0 to 20, such compounds include acetic acid; propionic acid; butanoic acid; pentanoic acid; hexanoic acid; heptanoic acid; octanoic acid; nonanoic acid; decanoic acid; undecanoic acid; lauric acid; tridecanoic acid; tetradecanoic acid; pentadecanoic acid; hexadecanoic acid; heptadecanoic acid; octadecanoic acid (stearic acid); nonadecanoic acid; and eicosonic acid.

(c) alkyl dicarboxylic acids having the formula $HOOC-(CH_2)_n-COOH$, wherein n ranges from 0 to 8, such as oxalic acid; malonic acid; succinic acid; glutaric acid; adipic acid; pimelic acid; suberic acid; azelaic acid; and sebacic acid;

(d) hydroxyalkyl carboxylic acids such as citric acid; tartaric acids; malic acid; mandelic acid; and 12-hydroxystearic acid;

(e) unsaturated alkyl carboxylic acids such as maleic acid; fumaric acid; and cinnamic acid;

(f) fused ring aromatic carboxylic acids such as naphthalenic acid; and anthracene carboxylic acid;

(g) cycloaliphatic acids such as cyclohexane carboxylic acid; cyclopentane carboxylic acid; furan carboxylic acids.

2) Organic sulfur acids including:

(a) sulfonic acids including:

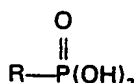
(1) benzenesulfonic acids such as benzenesulfonic acid; phenolsulfonic acid; dodecylbenzenesulfonic acid; benzenedisulfonic acid; benzenetrisulfonic acids; para-toluenesulfonic acid; and

(2) alkyl sulfonic acids such as methane sulfonic acid; ethane sulfonic acid; butane sulfonic acid; butane disulfonic acid; sulfosuccinate alkyl esters such as dioctyl succinyl sulfonic acid; and alkyl polyethoxy-succinyl sulfonic acid; and

(b) alkyl sulfates such as the lauryl half ester of sulfuric acid and the octadecyl half ester of sulfuric acid.

3) Organophosphorus acids including:

(a) phosphonic acids having the formula:



wherein R is an aryl group or alkyl having 1 to 22 carbon atoms;

(b) phosphinic acids having the formula:



wherein R is an aryl group or alkyl group having 1 to 22 carbon atoms, such as dicyclohexyl phosphinic acid; dibutyl phosphinic acid; and dilauryl phosphinic acid;

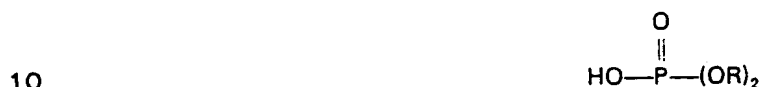
(c) thiophosphinic acids having the formula:



5 wherein R is an aryl group or alkyl group having 1 to 22 carbon atoms such as di-iso-butyl dithiophosphinic acid; dibutyl dithiophosphinic acid; dioctadecyl dithiophosphinic acid;

(d) phosphites, that is diesters of phosphorous acid having the formula: $\text{HO}-\text{P}(\text{OR})_2$; wherein R is an alkyl group having 1 to 22 carbon atoms such as dioctadecylphosphite;

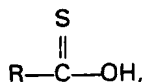
(e) phosphates, that is diesters of phosphoric acid having the formula:



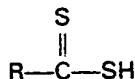
wherein R is an alkyl group having 1 to 22 carbon atoms, such as dioctadecyl phosphate.

4) Phenols such as phenol; hydroquinone; t-butylcatechol; p-methoxyphenol; and naphthols.

5) Thioacids having the formulae:



and



wherein R is an aryl group or alkyl group having 1 to 22 carbon atoms, such as thiosalicylic acid; thiobenzoic acid; thioacetic acid; thiolauric acid; and thiostearic acid.

20 6) Amino acids such as the naturally occurring amino acids and derivatives thereof such as 6-aminohexanoic acid; 12-aminododecanoic acid; N-phenylglycine; and 3-aminocrotonic acid.

7) Polymeric acids prepared from acidic monomers wherein the acidic functions remains in the polymer chain such as low molecular weight acrylic acid polymers and copolymers; styrene maleic anhydride copolymers.

25 8) Miscellaneous acids and acid salts such as ferrocyanide; ferricyanide; sodium tetraphenylborate; phosphotungstic acid; phosphosilicic acid, or any other such anion which will form a tight ion pair with an organic cation, i.e., any such anion which forms a water insoluble precipitate with an organic cation.

30 For convenience of handling it is preferred that the total organic content of the organophilic clay reaction products of this invention should be less than about 50% by weight of the organoclay. While higher amounts are usable the reaction product is difficult to filter, dry and grind.

A sufficient amount of organic cation is employed to satisfy the cation exchange capacity of the clay and the cationic activity of the organic anion. Additional amounts of cation above the sum of the exchange capacity of the clay and anion are optional. For example, smectite-type clays require at least 90 milliequivalents of organic cation to satisfy at least a portion of the total organic cation requirement. Use of amounts from 80 to 200 M.E., and preferably 100 to 160 M.E. are acceptable. At lower milliequivalents ratios, an incomplete reaction will occur resulting in an ineffective gellant.

40 The amount of organic anion added to the clay should be sufficient to impart to the organophilic clay the enhanced dispersion characteristic desired. This amount is defined as the milliequivalent ratio which is the number of milliequivalents (M.E.) of the organic anion in the organoclay per 100 grams of clay, 100% active clay basis. The anion milliequivalent ratio should preferably range from 5 to 100 and preferably 10 to 50.

The organic anion is preferably added to the reactants in the desired milliequivalent ratio as a solid or solution in water under agitation to effect a macroscopically homogenous mixture.

45 Smectite-type clays occur naturally or are prepared synthetically. Suitable clays include montmorillonite, bentonite, beidellite, hectorite, saponite, and stevensite. In particular smectite-type

clays should have a cation exchange capacity of at least 75 milliequivalents per 100 grams of clay. Particularly desirable types of clay are the naturally-occurring Wyoming varieties of bentonite and hectorite, a swelling magnesium-lithium silicate clay. Suitable synthetic clays may be synthesized by conventional means including pneumatolitic and hydrothermal methods.

5 The clays, especially the bentonite type clays, are preferably converted to the sodium form if they are not already in this form. This can conveniently be done by preparing an aqueous clay slurry and passing the slurry through a bed of cation exchange resin in the sodium form. Alternatively, the clay can be mixed with water and a soluble sodium compound such as sodium carbonate and sodium hydroxide followed by shearing the mixture with a pugmill or extruder. 5

10 The cation exchanger capacity of the smectite-type clays can be determined by the ammonium acetate method. 10

The clay is preferably dispersed in water at a concentration from about 1 to 80% and preferably about 2% to 20%, and more preferably about 2% to 7%. The slurry is agitated prior to reaction.

15 The organic cationic compounds of the invention were prepared by standard prior art methods starting with an amine having the desired number of long chain alkyl groups bonded to the nitrogen atom. This long chain alkyl amine was then reacted by reductive alkylation with an aldehyde and/or by nucleophilic displacement of an alkyl halide to form the desired quaternary ammonium compound. 15

20 The fluid of this invention may contain the aqueous phase includes aqueous solutions of inorganic salts such as sodium chloride and calcium chloride. While addition of these salts is optional, such salts increase the osmotic pressure of the water phase of the formations containing hydratable clays. 20

25 Then a concentration of water in the fluid is determined by factors such as fluid weight requirements, flow properties desired, bottom-hole temperatures and the operational requirements of drilling, coring, or completion. In general, it is preferable to employ a volume percent of water ranging from about 2 to about 50%. This range renders the oil-base fluid fire-resistant upon exposure to temperatures that would ignite the oil. In addition, the fluid has excellent tolerance to water contamination; and fluid flow properties can be controlled at values comparable to those of water-based fluids. 25

30 Conventional emulsifiers should be employed for the water-in-oil phase and may be employed for the non-aqueous fluid. The amount of emulsifier employed is primarily dependent upon the amount of water present and the extent of emulsification desired. Generally from 2 to 30 lbs. per barrel and preferably from 5 to 20 lbs. per barrel have been found satisfactory to achieve the necessary gel strengths and filtration control. 30

35 The compositions may optionally contain conventional weighting agents such as barite for controlling fluid density between 7.5 and 22 lb/gal as well as fluid loss control agents. 35

The smectite-type clays used in the Examples were hectorite and Wyoming bentonite. The clay was slurried in water and centrifuged to remove essentially all of the non-clay impurities which may amount to 10% to about 50% of the starting clay composition. The Wyoming bentonite clay slurry was passed through a bed of cation exchange resin to convert it to the sodium form.

40 Examples 1 to 4 demonstrate the preparation of various organic cationic compounds which compounds may be used as reactants with an organoclay to form the organophilic clay reaction products of this invention. 40

The organic cationic compounds exemplified are representative of the cations of the invention and are not intended to be inclusive of only operative compounds.

45 The following examples are given to illustrate the invention, but are not deemed to be limiting thereof. All percentages given are based upon weight unless otherwise indicated. Plastic viscosity, yield point, and ten second gels were measured by the procedure described in API RP 13B, American Petroleum Institutes Standard Procedure for Testing Fluids, 6th Ed., April 1976. Barrels (bbl) and gallons are U.S. measures. 45

Example 1

50 Allyl methyl di(hydrogenated-tallow) ammonium chloride (AM2HT). 824.7 g methyl di(hydrogenated-tallow) amine, 350 ml isopropyl alcohol, 250 g NaHCO₃, 191.3 gm. allyl chloride, and 10 gm. allyl bromide (as a catalyst) were mixed in a 4-liter reaction vessel equipped with a condenser. The mixture was heated and allowed to reflux. A sample was removed, filtered, and titrated with HCl and NaOH. The reaction was considered complete as there was 0.0% amine HCl and 1.8% amine. The final analysis of the AM2HT showed an effective gram molecular weight of 831.17. 55

Example 2

60 A 3% clay slurry (sodium form of Wyoming bentonite) was heated to 60°C with stirring. 4.8637 g (M.E. Ratio—22.5) of an organic anionic compound, sodium benzoate (M.W. 144.11) was dissolved in water. The organic anion solution was added to the clay slurry and reacted for 10 minutes at 60°C. 136.89 g (M.E. ratio—122.5) ethanol methyl di (hydrogenated-tallow) ammonium chloride [EM2HT] (M.W. 745) (Armak Co., Division of Akzona Corp.) is dissolved in a 50% 2-propanol aqueous solution. The cation solution was added and stirred for 45 minutes at 60°C. The organoclay 60

(EM2HT/benzoate/bentonite) was collected on a vacuum filter. The filter cake was washed with hot water and dried at 60°C. The dried organoclay was ground using a hammer mill to reduce the particle size and then sieved through a U.S. Standard 200 mesh screen.

Example 3

- 5 A 3% clay slurry (sodium form of Wyoming bentonite) was heated to 60°C. with stirring. 7.83 g (M.E. ratio—22.5) of an organic anionic compound, p-Phenolsulfonic acid sodium salt (M.W. 232.19) was dissolved in water. The organic anion solution was added to the clay slurry and reacted for 10 minutes at 60°C. 134.42 g (M.E. ratio—122.5) benzyl methyl di(hydrogenated-tallow) ammonium chloride BM2HT was dissolved in a 50% 2-propanol aqueous solution. The cation solution was added and stirred for 45 minutes at 60°C. The organoclay (BM2HT/p-phenolsulfonate/bentonite) was collected on a vacuum filter. The filter cake was washed with hot water and dried at 60°C. The dried organoclay is ground using a hammer mill to reduce the particle size and then sieved through a U.S. Standard 200 mesh screen.

Example 4

- 15 A 3% clay slurry (sodium form of Wyoming bentonite) was heated to 60°C. with stirring. 5.40 g (M.E. Ratio—22.5) of an organic anionic compound, sodium salt of salicylic acid (M.W. 160.11) was dissolved in water. The organic anion solution was added to the clay slurry and reacted for 10 minutes at 60°C. 134.72 g (M.E. ratio—122.5) of AM2HT prepared in Example 1 is dissolved in a 50% 2-propanol aqueous solution. The cation solution was added and stirred for 45 minutes at 60°C. The organoclay (AM2HT/salicylate/bentonite) was collected on a vacuum filter. The filter cake was washed with hot water and dried at 60°C. The dried organoclay was ground using a hammer mill to reduce the particle size and then sieved through a U.S. Standard 200 mesh screen.

Examples 5—9

- 25 0.63 bbl of diesel oil, 8 pounds emulsifier (Invermul, NL Industries, Inc.), 8 pounds filtration control, amine lignite (Duratone HT, NL Industries, Inc.), 4 pounds lime, and 0.11 bbl. of water was stirred for 20 minutes.

- 30 22 pounds of calcium chloride, 325 pounds of barite (Baroid/NL Industries, Inc.) and 5 pounds of the three bentonite clay thickeners prepared in Examples 2—4 in addition to commercial products dimethyl di(hydrogenated-tallow) ammonium chloride (2M2HT)/bentonite and benzyl methyl di(hydrogenated-tallow) ammonium chloride (BM2HT)/bentonite.

The mixed fluid was tested at 95°F. for standard rheology data and the results are shown in Table 2. None of the Examples settled following stirring:

Table 2

Example No.	Gellant Compound	Yield point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²
5	EM2HT/benzoate/bentonite	16	8	12
6	BM2HT/p-phenolsulfonate/bentonite	24	14	16
7	AM2HT/salicylate/bentonite	18	10	14
8	2M2HT/bentonite	30	16	19
9	BM2HT/bentonite	24	14	18

- 45 The unstirred batches of Examples 5—9 were rolled at 150°F for 16 hours and no settling was noted in any Example. The fluid was stirred for 25 minutes and tested at 88°F for standard rheology data as in Example 5. The results are shown in Table 3 below. None of the Example settled following stirring.

Table 3

Example No.	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²
5	14	7	10
6	22	14	17
7	16	11	13
8	20	13	18
9	21	14	19

350 ml. batches of fluid consisting of 0.60 of diesel oil, 8 pounds emulsifier (Invermul, NL Industries, Inc.), 8 pounds amine lignite filtration control (Duratone, NL Industries, Inc.), 5 pounds lime, 0.20 bbl of 11.0 ppg calcium chloride, and 320 pounds of barite (Baroid, NL Industries, Inc.) were admixed, stirred for 15 minutes in a Hamilton Beach mixer and cooled to 28°F in an ice bath. A 6 lb/bbl concentration of gellants EM2HT/benzoate/bentonite, BM2HT/p-phenolsulfonate/bentonite and AM2HT/salicylate/bentonite produced in Example 2—4 in over a 5 minute period at low shear with a Lightnin mixer. The cold examples in a viscometer cup, were placed on a Fann 35 viscometer and stirred at 600 rpm while the temperature rose to 70°F. The batches were then placed in a preheated cup jackets set at 125°F and allowed to heat to 110°F. The plastic viscosity, yield point and 10-sec gel were measured at every 5°F increment between 30 to 70° and at every 10°F increment between 70 to 110°F. The results of the measurements are presented in Figure 1.

Examples 15—19 at 115°F were stirred for 15 minutes in a Hamilton Beach mixer and cooled to 80°F and tested as with Example 5. The results are presented in Table 4 below.

Table 4

Example No.	Gellant Compound	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²
10	EM2HT/benzoate/bentonite	40	17	20
11	BM2HT/p-phenolsulfonate/bentonite	51	27	29
12	AM2HT/salicylate/bentonite	54	23	30
13	2M2HT/bentonite	50	21	26
14	BM2HT/bentonite	50	23	28

Examples 20—14

Batches of fluids consisting of 0.41 bbl of diesel oil and 12 pounds of gellant clays prepared in Examples 2, 3, 4 and 5 in addition to 2M2HT/bentonite and BM2HT/bentonite which were prepared without anionic reactants were admixed and stirred for five minutes in a Hamilton Beach mixer at low speed. 0.41 bbl of diesel oil, 18 pounds asphalt (Baroid Asphalt, NL Industries, Inc.) and 0.275 pounds of barite, (Baroid, NL Industries, Inc.) were admixed with the prepared batches above and stirred for 15 minutes in a Hamilton Beach mixer.

350 ml samples of Examples 20 through 24 were tested for rheological properties as in Example 5 at 93°F. The results are presented in Table 5 below.

Table 5

Example No.	Gellant Compound	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²
15	EM2HT/benzoate/bentonite	15	7	27
16	BM2HT/p-phenolsulfonate/bentonite	17	7	31
17	AM2HT/salicylate/bentonite	15	4	11
18	2M2HT/bentonite	54	34	74
19	BM2HT/bentonite	25	11	40

350 ml samples of Example 15 through 19 were hot rolled at 150°F for 16 hours. After cooling the batches to 80°F, settling of solids were checked prior to measurement of rheological properties as in Example 5 at 93°F. The results are shown in Table 6 below.

Table 6

Example No.	Gellant Compound	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²
15	EM2HT/sodium benzoate/bentonite	37	10	40
16	BM2HT/p-phenolsulfonate/bentonite	37	13	55
17	AM2HT/salicylate/bentonite	52	17	78
18	2M2HT/bentonite	91	55	100
19	BM2HT/bentonite	69	39	108

Mud cake and filtrates were stirred back into the respective samples and the batches were aged for 16 hours at 350°F.

Each batch was cooled to 80°F and checked for solids settling. The batches were stirred for 5 minutes and tested as with Example 5. The results are shown in Table 7 below.

Table 7

Example No.	Gellant Compound	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²	
5	15 EM2HT/benzoate/bentonite	68	10	34	5
	16 BM2HT/p-phenolsulfonate/bentonite	70	14	51	
10	17 AM2HT/salicylate/bentonite	62	15	30	10
	18 2M2HT/bentonite	120	45	82	
	19 BM2HT/bentonite	99	41	78	

Examples 20 to 24

350 ml. batches of fluids consisting of 0.69 bbl of diesel oil, 6 pounds emulsifier (EZ mul, NL Industries, Inc.), 0.12 bbl of water, 225 pounds of barite (Baroid, NL Industries, Inc.), 24 pounds of calcium chloride and 6 pounds of gellant clays EM2HT/benzoate/bentonite, BM2HT/p-phenolsulfonate/bentonite and AM2HT/salicylate/bentonite prepared in Examples 2—4 respectively in addition to 2M2HT/bentonite and BM2HT/bentonite described in Example 5 were admixed and stirred for 20 minutes in a Hamilton Beach mixer.

350 ml. batches of Examples 20 through 24 were tested at 88°F for rheological properties as in Example 5. The results are presented in Table 8 below.

Table 8

Example No.	Gellant Compound	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²	
25	20 EM2HT/benzoate/bentonite	9	4	6	25
	21 BM2HT/p-phenolsulfonate/bentonite	8	4	6	
	22 AM2HT/salicylate/bentonite	9	4	5	
30	23 2M2HT/bentonite	9	5	6	30
	24 BM2HT/bentonite	8	4	5	

350 ml sample of Example 20 through 24 were hot rolled at 150°F for 16 hours. After cooling the batches to 80°F, settling of solids was checked prior to measurement of rheological properties as in Example 5 at 84°F. The results are shown in Table 9 below.

Table 9

Example No.	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²	
35				35
40	20 9	5	5	40
	21 9	5	7	
	22 10	5	8	
	23 15	8	14	
	24 9	4	5	

Mud cake and filtrate were stirred back into the respective samples and the batches were aged for 16 hours at 350°F.

Each batch was cooled to 80°F and checked for solids settling. The batches were stirred for 5 minutes and tested as with Example 5. HT-HP filtrates were conducted on each batch at 350°F. The results are shown in Table 10 below.

Table 10

	Example No.	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²	
5	20	10	5	5	5
	21	6	4	5	
	22	9	4	5	
	23	12	5	6	
10	24	8	4	5	10

Examples 25—29

350 ml. batches of a fluid consisting of 0.63 bbl of diesel oil, 8 pounds emulsifier (Invermul, NL Industries, Inc.), 0.11 bbl of water, 325 pounds of barite (Baroid, NL Industries, Inc.), 8 pounds filtration aid (Duratone—NL Industries, Inc.), 22 pounds of calcium chloride, 4 pounds lime and 9 pounds of gellant clays. EM2HT/benzoate/bentonite, BM2HT/p-phenolsulfonate/bentonite, and AM2HT/salicylate/bentonite prepared in Example 2—4 respectively, commercial clays

2M2HT/bentonite, BM2HT/bentonite described in Example 5 above and an additional commercial clay. 350 ml samples of Examples 25 through 29 were tested at 92°F for rheological properties as in Example 5. The results are presented in Table 11.

Table 11

	Example No.	Gellant Composition	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²	
25	25	EM2HT/sodium benzoate bentonite	40	14	8	25
	26	BM2HT/p-phenol sulfonic acid bentonite	55	28	33	
	27	AM2HT/salicylic acid bentonite	43	18	20	
	28	2M2HT/bentonite	60	22	33	
	29	BM2HT/bentonite	51	24	28	

30 The batches were aged for 16 hours at 300°F, cooled to 80°F, checked for solids settling. The batches were stirred for 10 minutes and tested as with Example 5 at 90°F. The results are shown in Table 12 below.

Table 12

	Example No.	Yield Point #/100ft ²	10 sec. Gel #/100ft ²	10 min. Gel #/100ft ²	
35	25	32	18	23	35
	26	29	23	28	
40	27	27	20	26	40
	28	34	18	26	
	29	26	24	29	

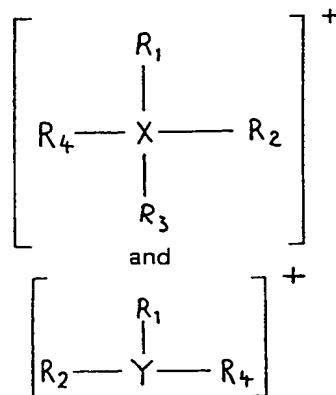
45 It will be obvious to one skilled in the art that the invention may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the following claims.

Claims

1. An oil-base fluid comprising an oil phase and from about 1 to 50 pounds per barrel of said fluid of an organophilic clay gellant comprising the reaction product of an organic cationic compound, an organic anion and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay such that an organic cation-organic anion complex is intercalated with the smectite-type clay and the cation exchange sites of the smectite-type clay are substituted with the organic cation.
2. An oil-base packer fluid which comprises an oil phase and from about 6 to 50 lbs. per barrel of said fluid of an organophilic clay gellant comprising the reaction product of an organic cationic compound, an organic anion and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay such that an organic cation—organic anion complex is

intercalated with the smectite-type clay and the cation exchange sites of the smectite-type clay are substituted with the organic cation.

3. In a method of insulating casing in a wellbore which comprises pumping an oil-base packer fluid in an annular space within said wellbore and thereafter gelling said packer fluid, the improvement comprises a packer fluid having an oil phase, and from about 6 to 50 pounds per barrel of said fluid of an organophilic clay gellant comprising the reaction product of an organic cationic compound, an organic anion and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay such that an organic cation-organic anion complex is intercalated with the smectite-type clay and the cation exchange sites of the smectite-type clay are substituted with the organic cation.
4. The gellant of Claim 1, 2, or 3, wherein the organic cation is selected from the group consisting of:



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- wherein X is nitrogen or phosphorus, Y is sulfur; R_1 is an alkyl group containing 8 to 60 carbon atoms; and R_2 , R_3 and R_4 are selected independently from the group consisting of hydrogen, a hydroxyalkyl group having 2 to 6 carbon atoms, alkyl groups containing 1 to 22 carbon atoms, aryl groups, aralkyl groups containing 1 to 22 carbon atoms on the alkyl chain, and mixtures thereof; and smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay, such that an organic cation-organic anion complex is intercalated with the smectite-type clay and the cation exchange sites of the smectite-type clay are substituted with the organic cation.
5. The gellant of Claim 1, 2 or 3 wherein R_1 is long chain alkyl group having 12 to 60 carbon atoms.

6. The gellant of Claim 5 wherein R_1 has from 12 to 22 carbon atoms.
7. The gellant of Claim 1, 2, or 3 wherein R_2 is selected from the group consisting of a β,γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, an aralkyl group and mixtures thereof.
8. The gellant of Claim 1, 2 or 3 wherein R_3 and R_4 are individually selected from the group consisting of a β,γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, an aralkyl group, an alkyl group having from 1 to 22 carbon atoms and mixtures thereof.

9. The gellant of Claim 1, 2 or 3 wherein the amount of said organic anion is from 5 to 100 milliequivalents per 100 g of said clay, 100% active clay basis.
10. The gellant of Claim 1, 2 or 3 wherein the amount of said organic cation is sufficient to satisfy the cation exchange capacity of the smectite-type clay and the cationic exchange capacity of the organic anion.

11. The gellant of Claim 1, 2 or 3 wherein the smectite-type clay is selected from the group consisting of hectorite, bentonite and mixtures thereof.
12. The gellant of Claim 1, 2 or 3 wherein R_2 is selected from a group consisting of a β,γ -unsaturated cyclic alkyl group, β,γ -unsaturated acyclic alkyl group having less than 7 carbon atoms, an acyclic β,γ -unsaturated alkyl group substituted with aromatic groups, an aromatic β,γ -unsaturated group substituted with aliphatic groups, and mixtures thereof.
13. The gellant of Claim 1, 2 or 3 wherein R_2 is a hydroxyalkyl group selected from a group consisting of cyclic groups, acyclic groups and mixture thereof, and said hydroxyl substitution is on C_2 to C_6 .

14. The gellant of Claim 6 wherein R_1 is a fatty acid group.
15. The gellant of Claim 1, 2, or 3 wherein the amount of said organic cation is from 100 to 130 milliequivalents per 100 grams of said clay, 100% active clay basis.
16. The fluid of Claim 1 wherein said fluid comprises additionally dispersed aqueous phase comprising from about 2 to about 50% by volume water.

17. The fluid of Claim 16 wherein said fluid comprises additionally a water-in-oil emulsifier.

18. The fluid of Claim 17 wherein said fluid comprises 2 to 30 lbs. per barrel water-in-oil emulsifier.

5 19. The packer fluid of Claim 2 or 3 wherein said fluid comprises additionally dispersed aqueous phase comprising from about 2 to about 50% by volume water.

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20. The packer fluid of Claim 19 wherein said fluid comprises additionally a water-in-oil emulsifier.

21. The packer fluid of Claim 20 wherein said fluid comprises additionally from about 2 to 30 pounds per barrel water-in-oil emulsifier.

10 22. The fluid of Claim 1 wherein said fluid is non-aqueous.

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23. The fluid of Claim 2 or 3 wherein said fluid is non-aqueous.

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